August 11, 2016

Advanced Solid Sorbents and Process Designs for Post-Combustion CO_2 Capture (DE-FE0007707)

RTI International

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Project Overview

Objective

Address the technical hurdles to developing a solid sorbent-based CO_2 capture process by transitioning a promising sorbent chemistry to a low-cost sorbent suitable for use in a fluidized-bed process

This project combined previous technology development efforts: RTI (process) and PSU (sorbent)

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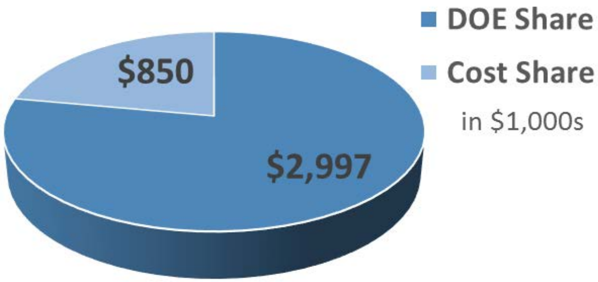


Period of Performance:

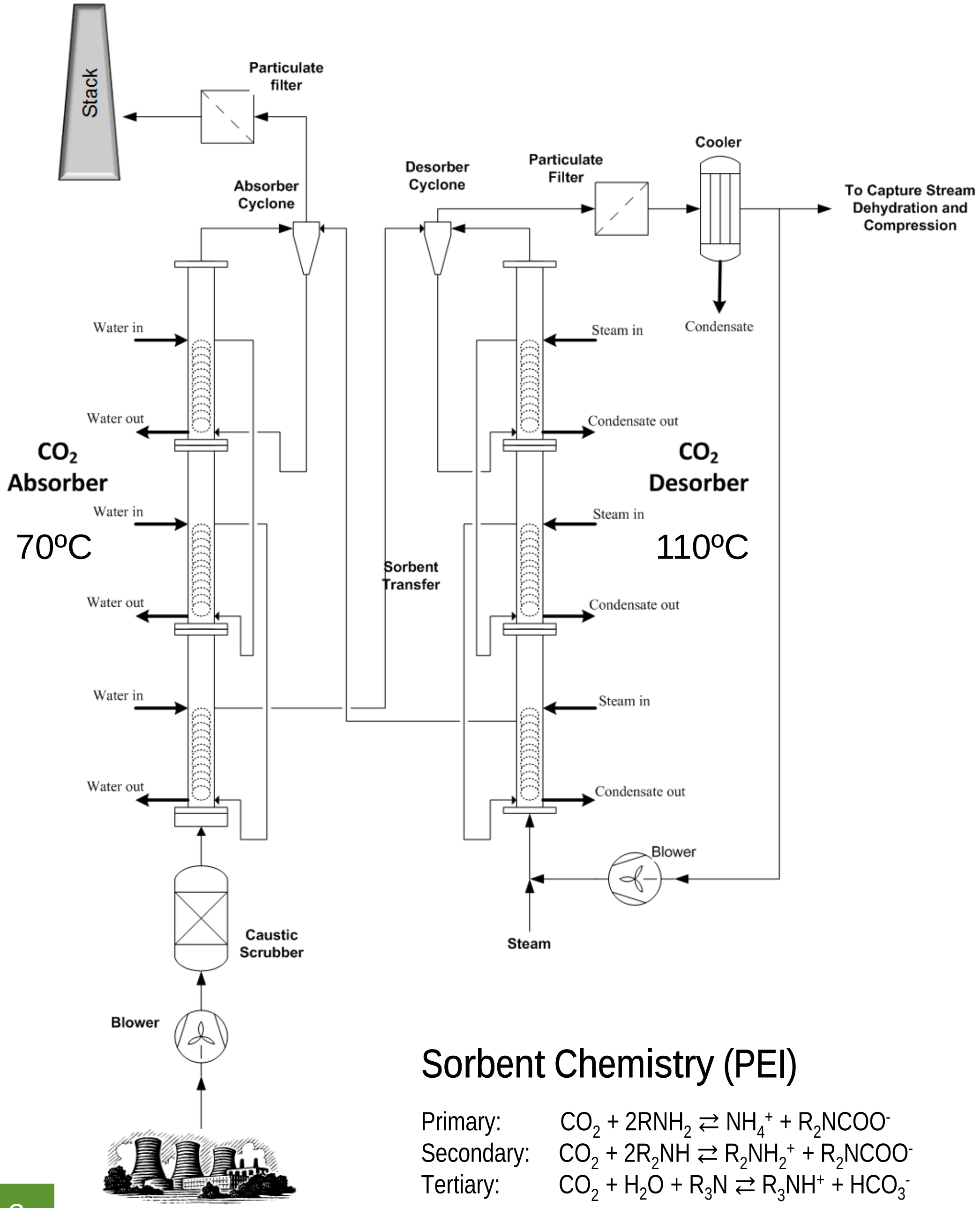
- 10/1/2011 to 12/31/2015

- Project management
- Process design
- Fluidized-bed sorbent

- PSU's EMS Energy Inst.
- PEI and sorbent improvement

- Masdar New Ventures
- Masdar Institute
- TEA of NGCC application

Solid Sorbent CO_2 Capture



Technology Features

- *Sorbent*: supported polyethyleneimine
- *Process*: fluidized, moving-bed

Advantages

- Potential for reduced energy loads and lower capital and operating costs
- High CO_2 loading capacity; higher utilization of CO_2 capture sites
- Relatively low heat of absorption; no heat of vaporization penalty
- Avoidance of evaporative emissions
- Superior reactor design for optimized and efficient CO_2 capture performance

Challenges

- Heat management / temperature control
- Solids handling / solids circulation control
- Physically strong / attrition-resistant
- Stability of sorbent performance

Sorbent Chemistry (PEI)

Primary: $CO_2 + 2RNH_2 \rightleftarrows NH_4^+ + R_2NCOO^-$

Secondary: $CO_2 + 2R_2NH \rightleftarrows R_2NH_2^+ + R_2NCOO^-$

Tertiary: $CO_2 + H_2O + R_3N \rightleftarrows R_3NH^+ + HCO_3^-$

Technical Approach & Scope

Previous Work	RTI's Project	Future Development		
< 2011	2011-15	2016 - 18	2018-22	> 2022
Proof-of-Concept / Feasibility		Pilot 0.5 - 5 MW (eq)	Demo ~ 50 MW	Commercial

Laboratory Validation (2011 – 2013)

Economic analysis

- ***Milestone:*** Favorable technology feasibility study

Sorbent development

- ***Milestone:*** Successful scale-up of fluidized-bed sorbent

Process development

- ***Milestone:*** Working multi-physics, CFD model of FMBR
- ***Milestone:*** Fabrication-ready design and schedule for single-stage contactor

Prototype Testing (2015)

Prototype Testing

- ***Milestone:*** Operational prototype capable of 90% CO_2 capture
- ***Milestone:*** Completion of extensive parametric and long-term testing campaigns

Updated Economics

- ***Milestone:*** Favorable technical, economic, environmental study (i.e. meets DOE targets)

Relevant Environment Validation (2013 – 2014)

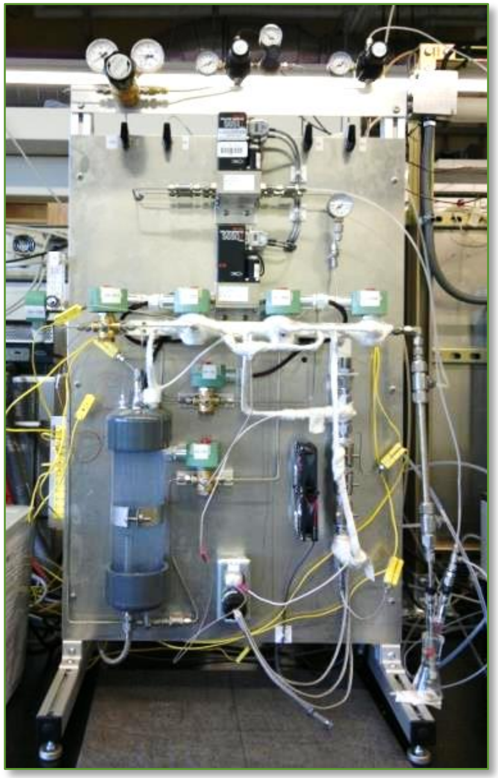
Process development

- ***Milestone:*** Fully operational bench-scale FMBR unit capable of absorption / desorption operation
- ***Milestone:*** Fabrication-ready design and schedule for high-fidelity, bench-scale FMBR prototype

Sorbent development

- ***Milestone:*** Successful scale-up of sorbent material with confirmation of maintained properties and performance

Test Equipment – PBR and vFBR

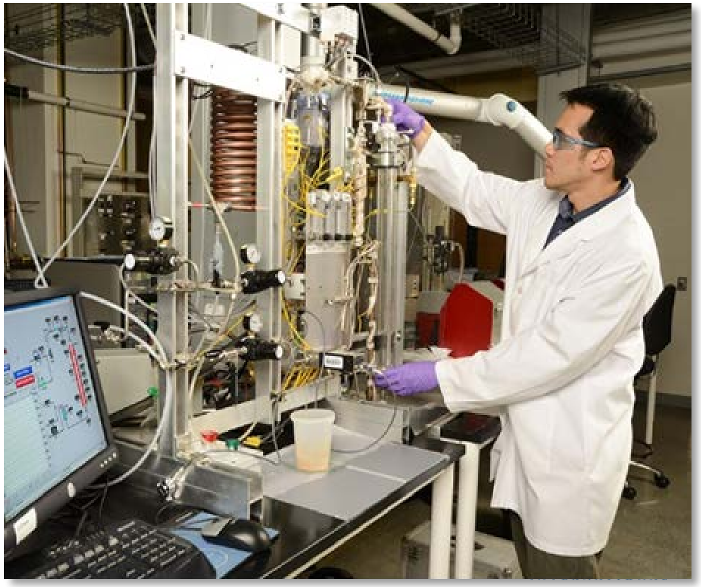


Packed-bed Reactor

- Fully-automated operation and data analysis; multi-cycle absorption-regeneration
- Rapid sorbent screening experiments
- Measure dynamic CO_2 loading & rate
- Test long-term effect of contaminants

- Verify (visually) the fluidizability of PEI-supported CO_2 capture sorbents
- Operate with realistic process conditions
- Measure △P and temperature gradients
- Test optimal fluidization conditions

“visual” Fluidized-bed Reactor



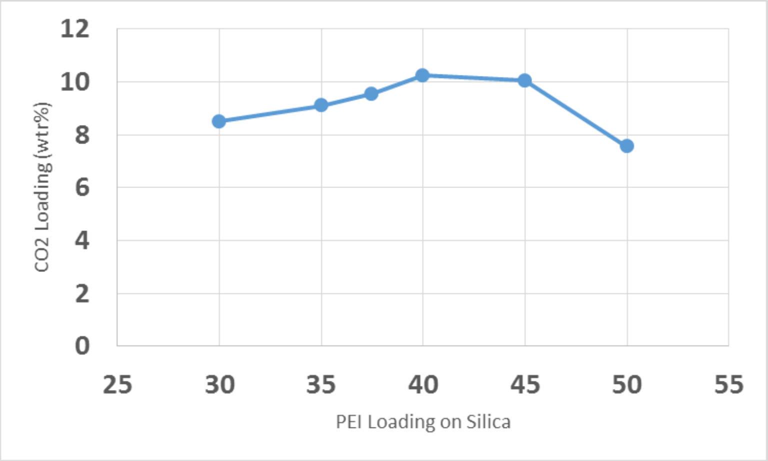
Sorbent Development & Scale-up

Objective

Improve the thermal and performance stability and production cost of PEI-based sorbents while transitioning fixed-bed MBS materials into a fluidizable form.

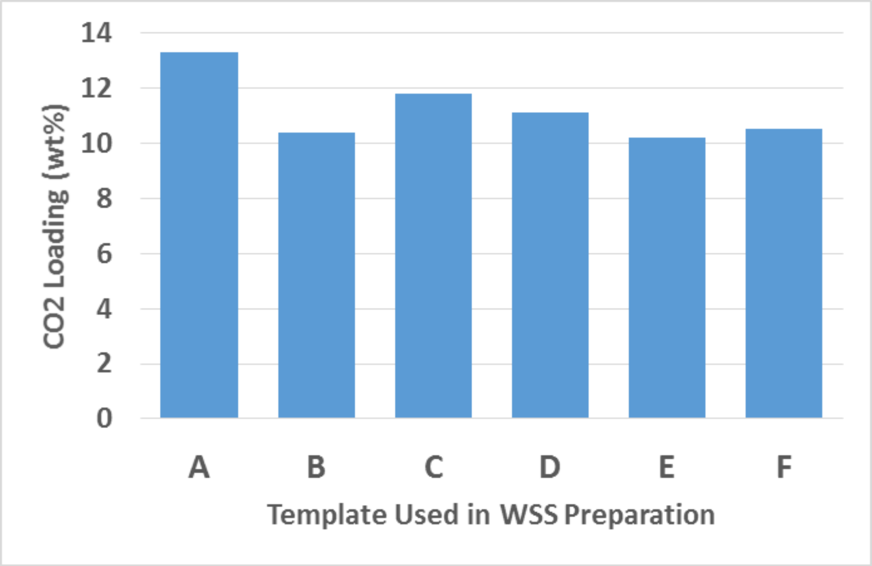
PEI-impregnated Silica ("Gen1")

- Stability improvements through addition of moisture and PEI / support modifications.
- Suitable low-cost, commercial supports identified (1000x cost reduction).
- Converted sorbent to a fluidizable form.
- Optimized Gen1 sorbent through: solvent selection; drying procedure; PEI loading %; regeneration method; support selection; etc.



Co-Precip Amine/Silica ("Gen2")

- Extremely stable sorbent, high CO_2 loadings (10 - 14 wt%).
- *Key benefits*: stability in liquid water, high CO_2 loadings, tailoring potential, diverse applications
- *Challenges*: density, physical strength, cost
- Mixed results with most promise identified in the use of blended amines and templates



Sorbent Scale-up

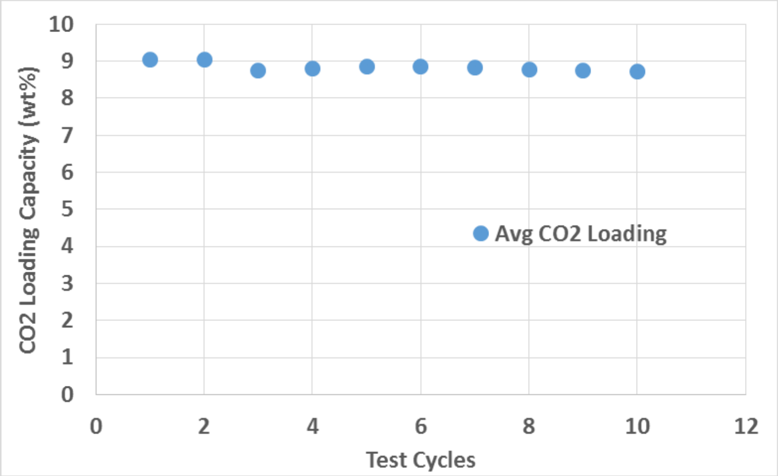
Initial Scale-up (150 kg)

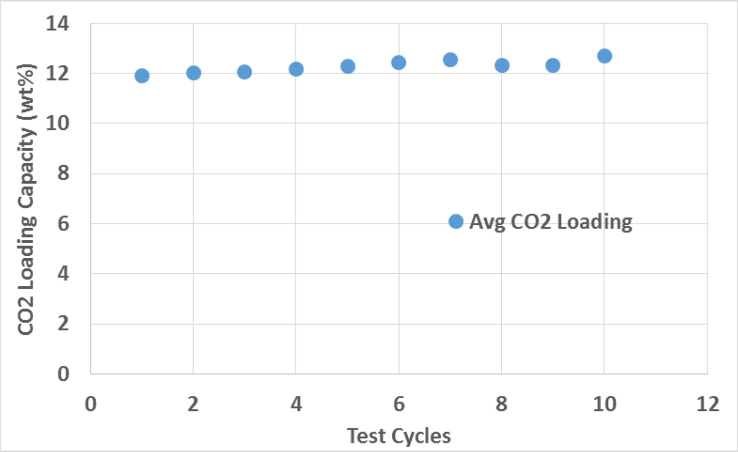
- 30 wt% PEI on commercially-available silica
- Scaled-up sorbent matches performance and properties of lab sorbent

	Amount	PEI loading	CO_2 Capacity	FBR test	PSD
Lab Sorbent	100+ g	30 %	8.5 wt%	Pass	75 – 250 um
Scaled-up Sorbent	150 kg	30 %	8.9 wt%	Pass	80 – 250 um

Sorbent Make-up Batch (100 kg) – following Oxidative Degradation

- Improved silica selection, optimized PEI loadings
- 6 months of bench-scale testing exhibited little to no degradation





Scale-up Batch (100 kg) – made for RTI's project with Norcem (cement application)

- Improved commercial preparation
- Sorbent exhibits improved CO_2 capture performance

RTI’s Bench-scale Prototype System

Specifications

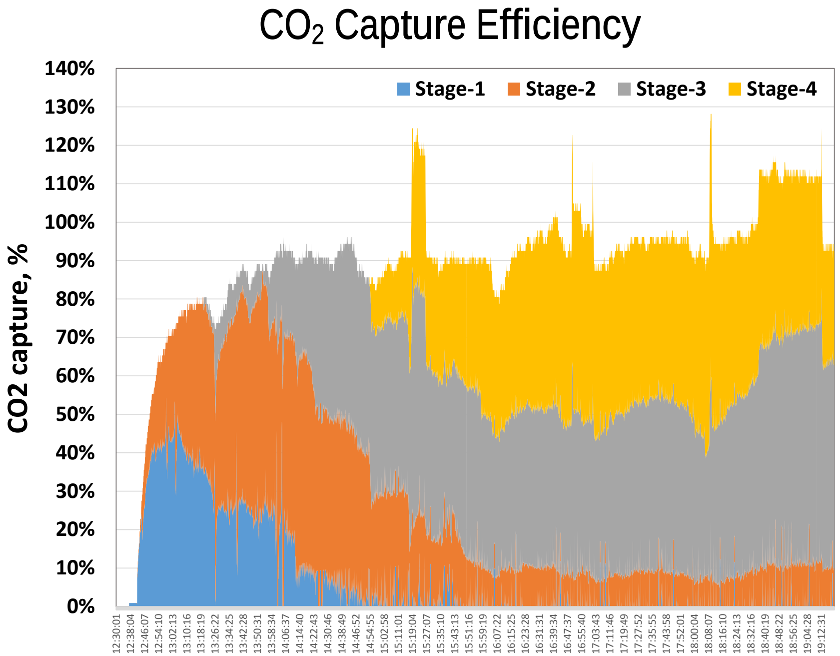
- *Flue gas throughput*: 300 and 900 SLPM
- *Solids circulation rate*: 75 to 450 kg/h
- *Sorbent inventory*: ~75 kg of sorbent
- *Adsorber temperature range*: 40 - 90˚C
- *Regenerator temperature range*: 100 - 130˚C
- *Heat exchange fluids*: CW in Adsorber; Steam in Regenerator
- *Footprint / Height*: 15’ x 5’ / 35’ H
- Pneumatic conveying of sorbent (Regen → Adsorber)
- Sorbent circulation rate controlled and monitored by measurement of the riser pressure drop

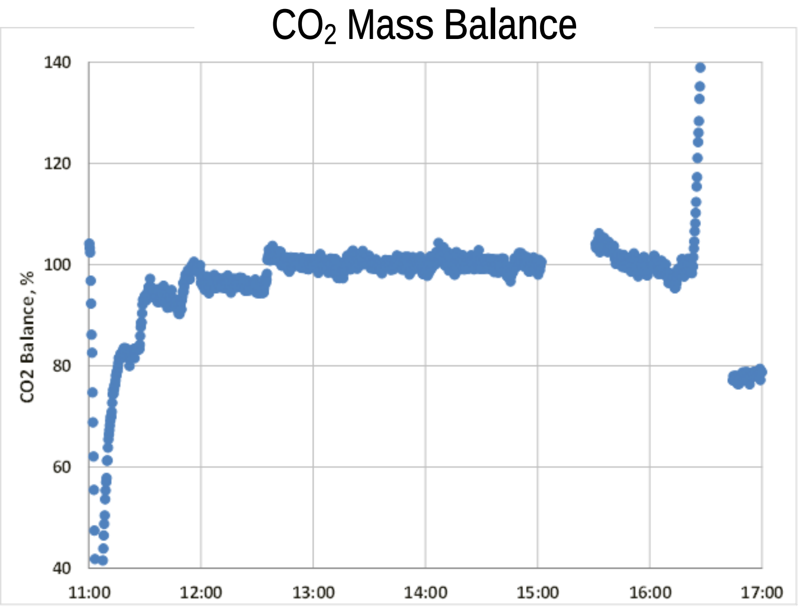
FG Compositon	CO_2	H_2O	N_2
	15 vol%	3 vol%	Balance

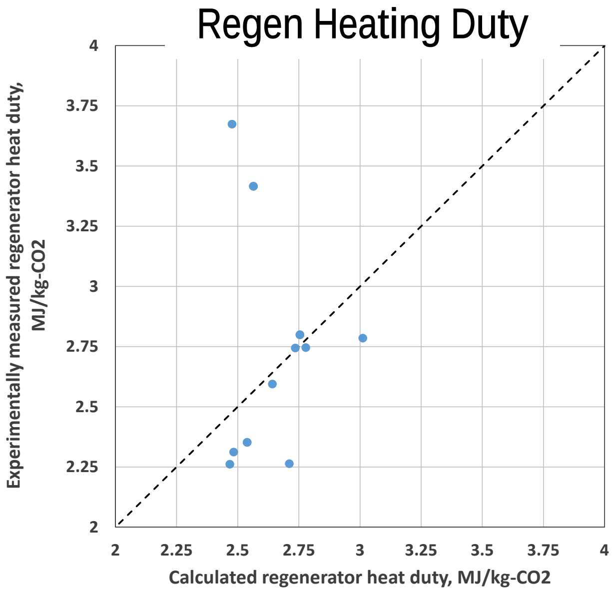
Operational improvements

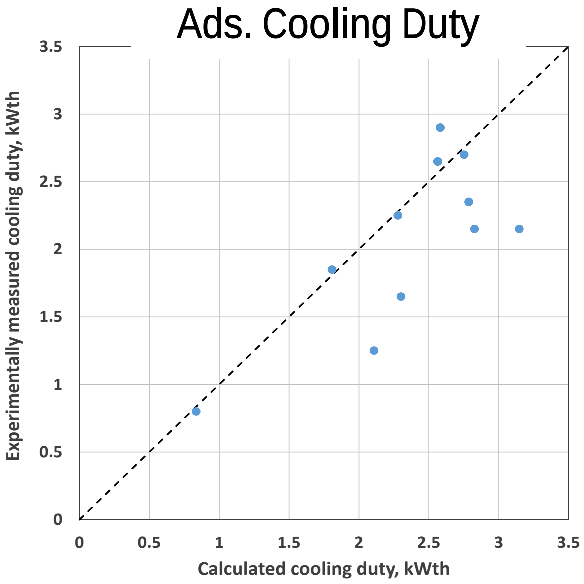
- Optimized loop seal aeration to maximize solids circulation
- Eliminated static electricity build-up which caused agglomeration
- Added pneumatic vibrators to downcomers, improving circulation
- Modified gas entrance arrangement to primary cyclone and added secondary cyclone to improve sorbent recovery
- Added larger downcomers for additional circulation reliability
- Full system reconfiguration:
  - Original configuration: 4-stage Ads, 1-stage Regen
  - Reconfiguration to 2-stage Ads, 2-stage Regen

Bench-scale System – Baseline Testing


CO$_2$ Capture Efficiency


CO$_2$ Mass Balance


Regen Heating Duty


Ads. Cooling Duty

Good correlation between calculated and experimentally measured heating and cooling duties (within +/- 10%)

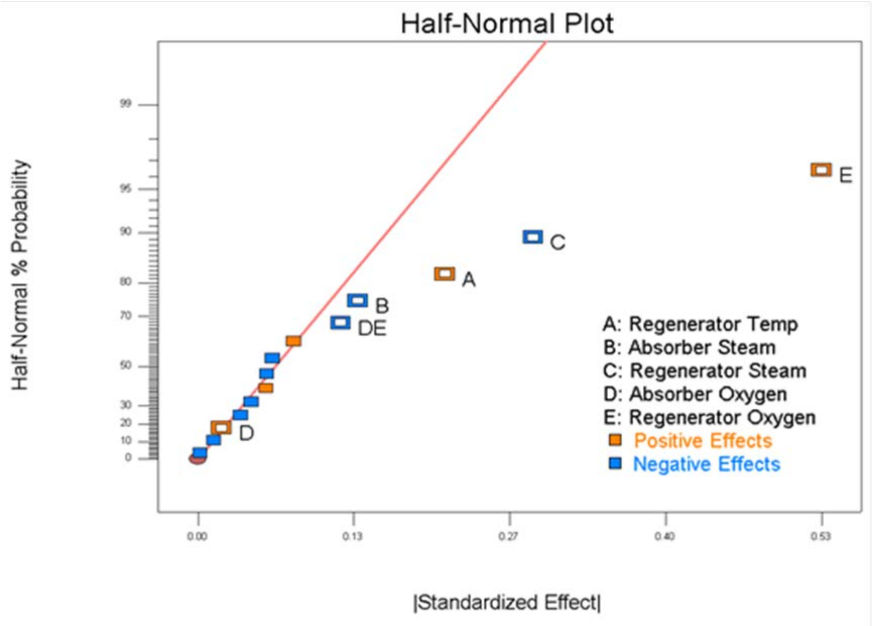
Oxidative Degradation

Challenge

Scaled-up sorbent was observed to have a steady decline in the sorbent's CO_2 capacity over several hundred hours of testing. CO_2 sorption capacity was impacted while fluidizability and other key physical parameters remained unaffected.

Potential Degradation Pathways

- PEI-leaching
- Dry flue gas
- Dry stripping gas
- Exposure to oxygen
- Combination of the conditions listed above.



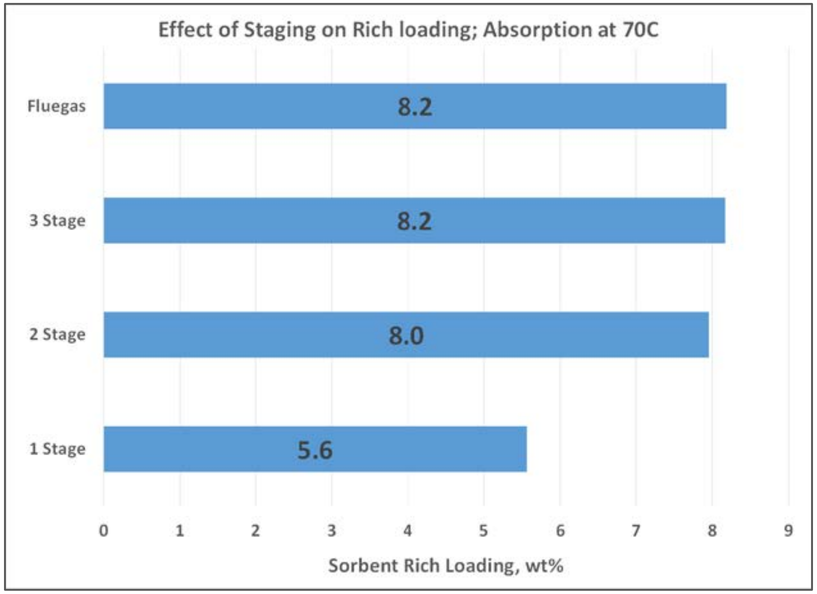
- A Design of Experiments (DoE) study was implemented and a half factorial test campaign for five parameters

Conclusions

- Two most important factors: O_2 concentration (i.e. exposure to O_2) and the temperature at which O_2 exposure occurs
- 3rd factor (absence of H_2O in stripping gas), important but is reversible
- Sorbent O_2 exposure at $< 70^{\circ}$C is acceptable
- Sorbent cooler is recommended when conveying with air

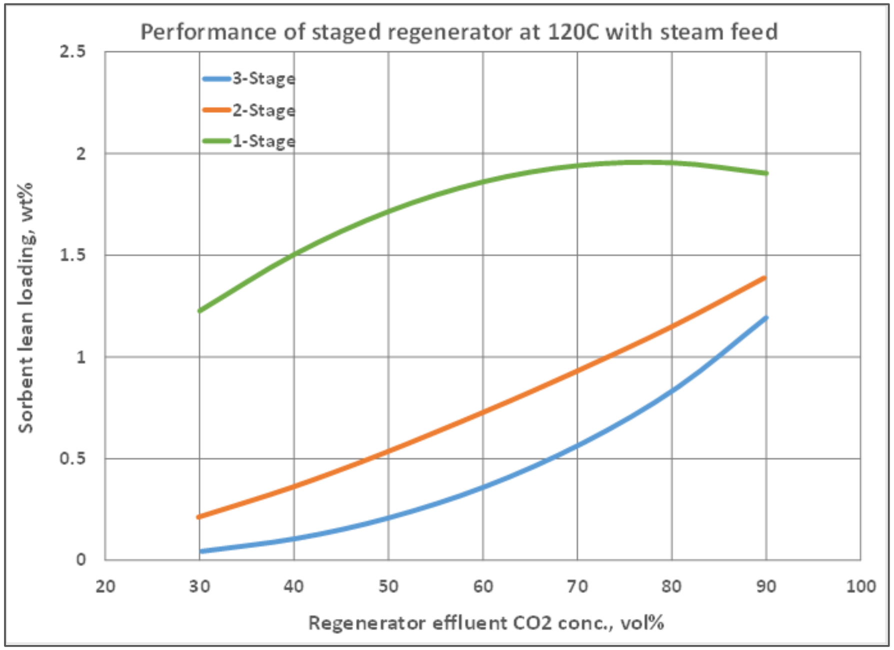
Reactor Staging

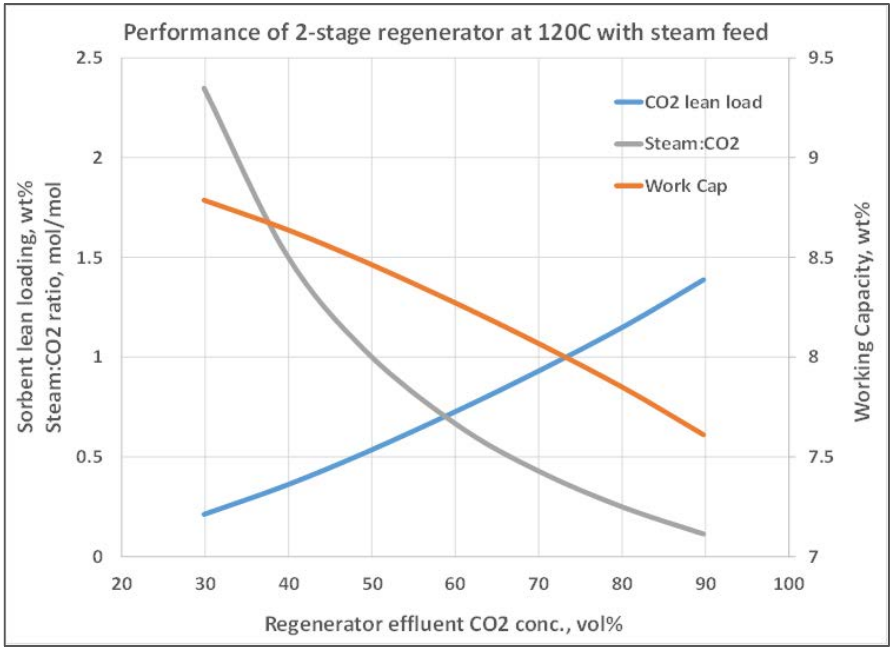
- Reactor staging required to maximize performance; well-mixed single-stage reactors limit achievable rich and lean loadings
- *Adsorber*: equilibrium loading calcs and experimental observations suggest 2 stages are sufficient
- *Regenerator*: 2 stages, minimum required



Bench system reconfiguration

- Removed bottom two adsorber stages which do not participate in CO_2 capture but act as dead/inert volume
- 2-stage Adsorber, 2-stage Regenerator

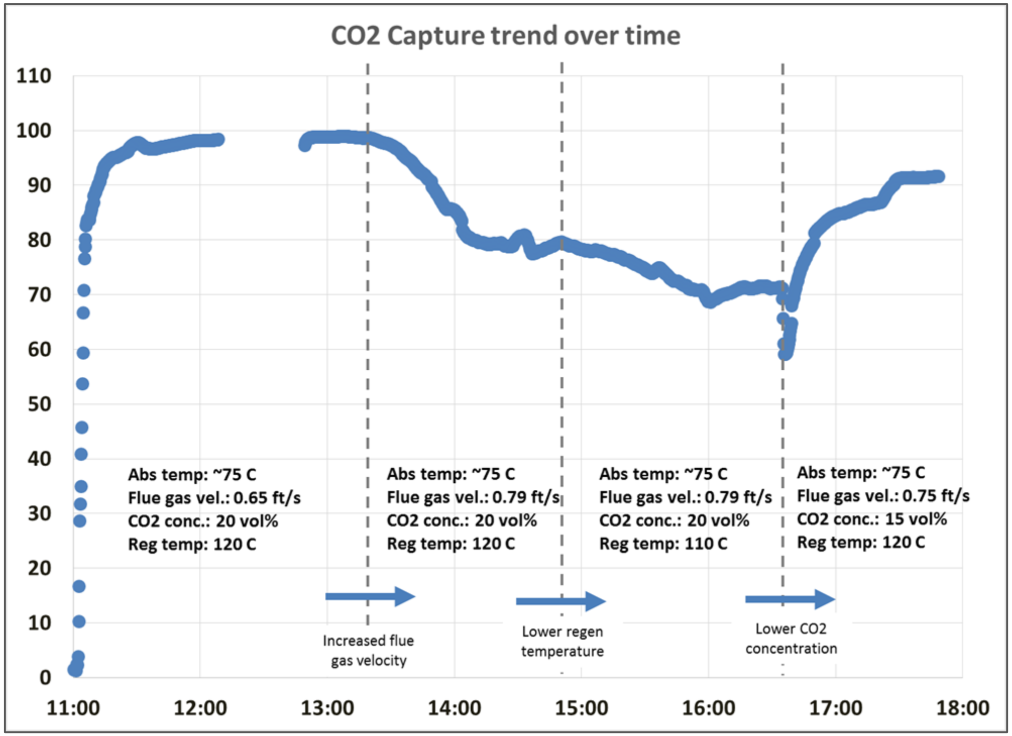


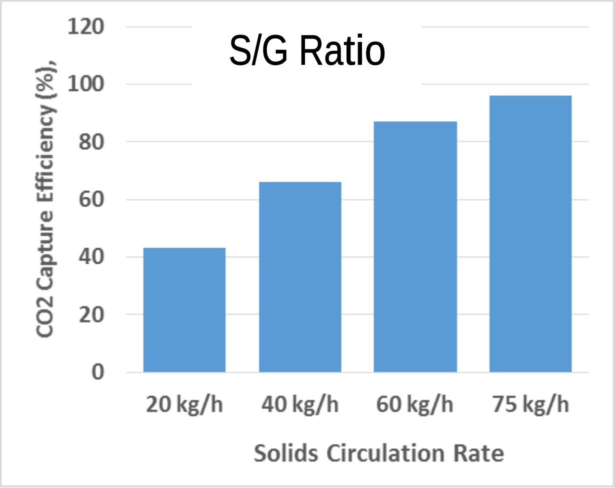


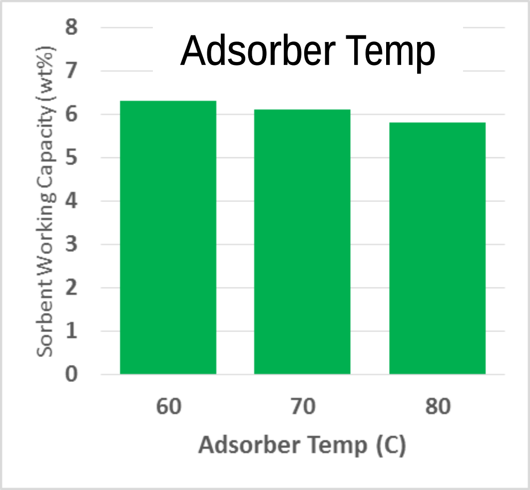
Bench-scale Prototype Testing

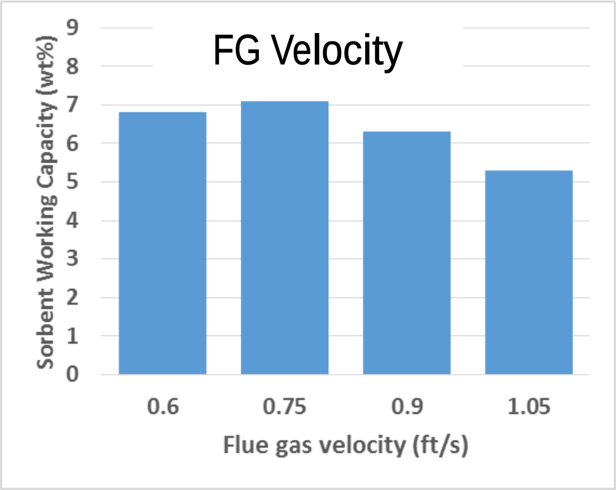
Highlights of prototype testing

- Cumulative testing: 1,000+ circulation hours; 420+ CO_2 capture hours.
- The sorbent is capable of rapid removal of CO_2 from the simulated flue gas
- Sustained 90% capture of the CO_2 in simulated flue gas stream is easily achieved
- Collected a wealth of performance data, identified how system performance varies due to process variables, and proved the reliable nature of bench-scale testing









Bench-scale Prototype Testing

Highlights of prototype testing

Heat Management

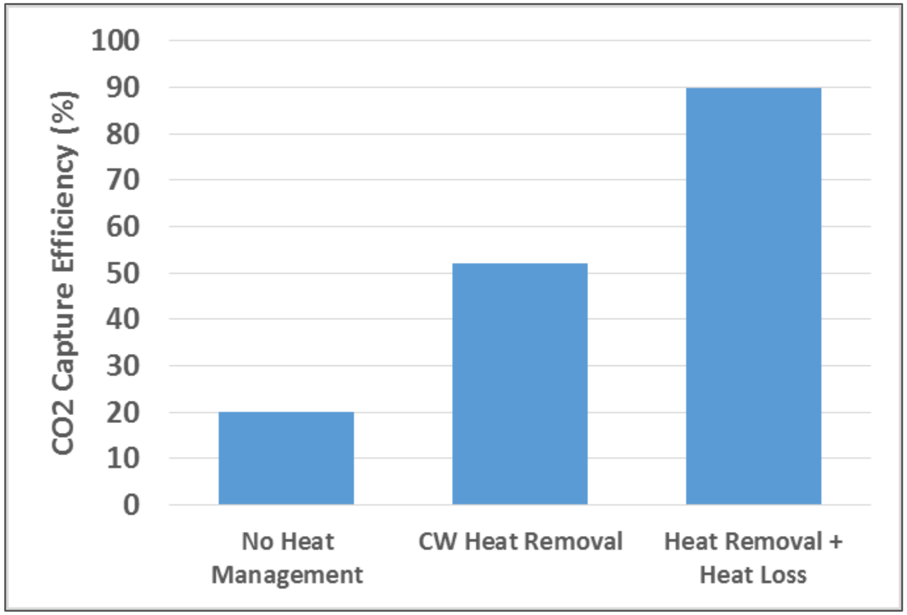
- Complicated by large heat losses to environment
- Able to demonstrate superior CO_2 capture performance with heat management

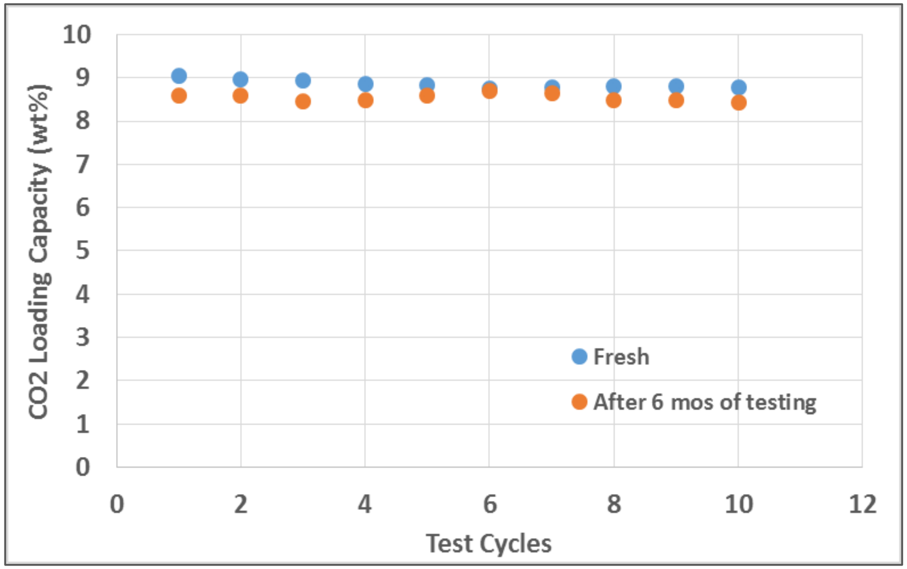
Operating Parameters

- Able to quantify system response and performance due to changing parameters
- Able to identify optimal conditions, balancing performance with other economic factors:
  - 70˚C Absorber temperature
  - 120˚C Regen temperature
  - > 1 ft/s FG velocity
  - Higher S/G ratios better, but energy and footprint impacts taken into account
  - Performance at a range of FG CO_2 concentrations was quantified

Sorbent Stability

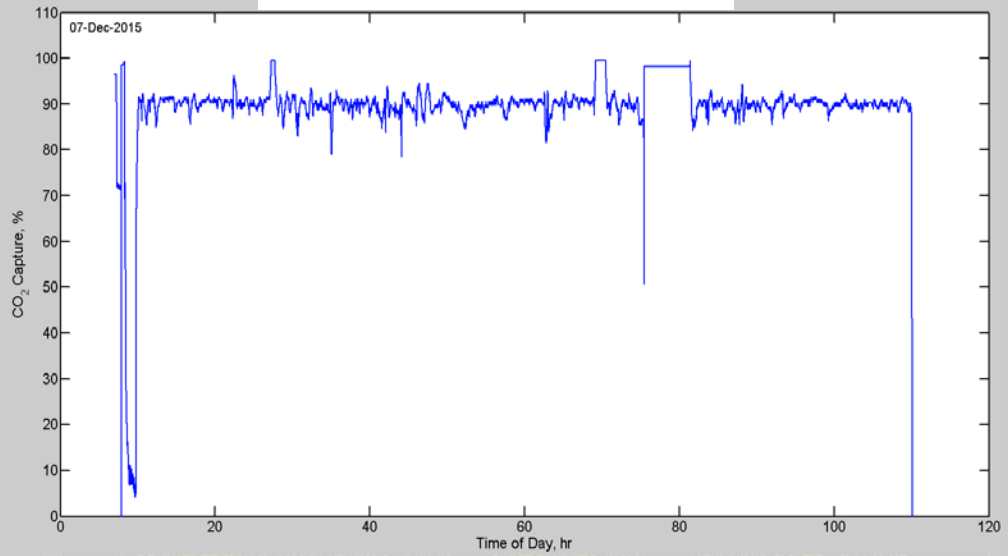
- CO_2 capacity stable between 8.5 – 9.0 wt% CO_2 loading after 6 months of testing
- Thermal and oxidative degradation avoided





Long-term Performance Testing

CO$_2$ Capture Efficiency



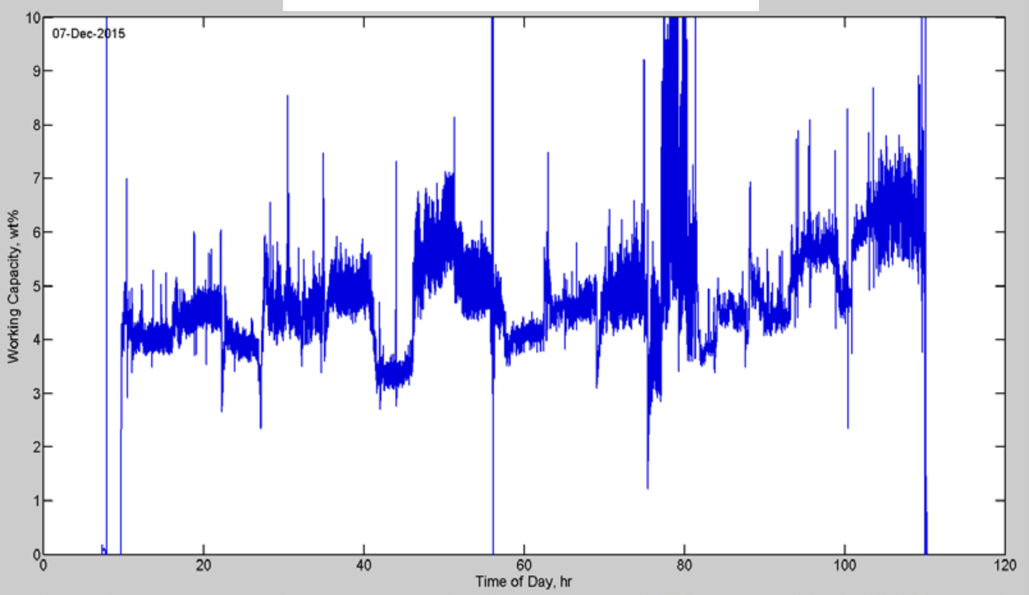
Long-term testing

- 100+ hr continuous testing, maintaining the performance target of 90% CO$_2$ capture while varying sorbent circulation rate
- Sorbent maintained CO$_2$ working capacity between 4 and 7 wt.%
- Desired set points for all process conditions and reactor settings were tightly controlled
- Robust nature of system proven

Other Observations / Lessons

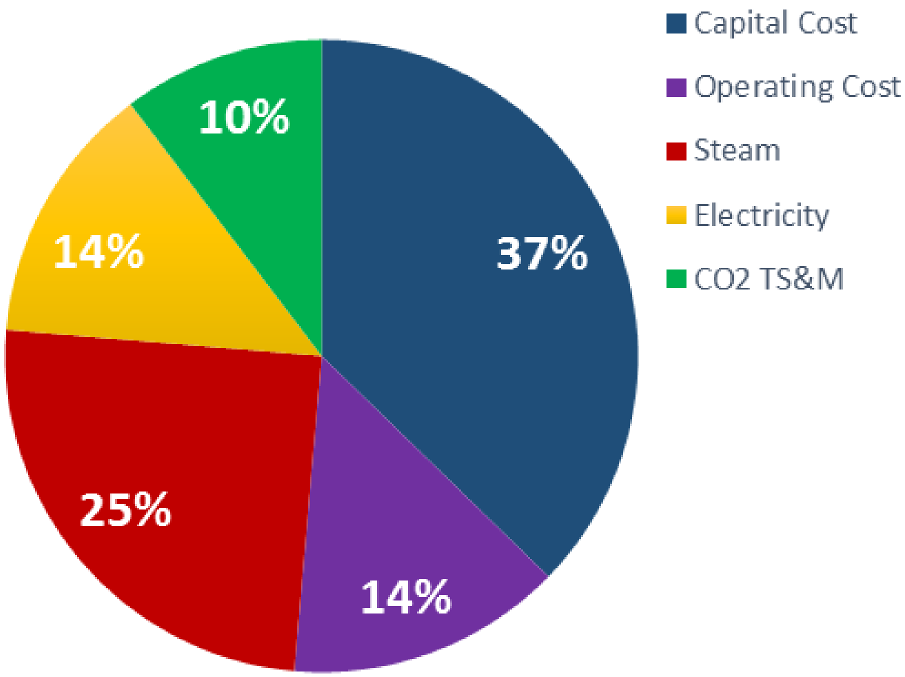
- Attrition-resistance of sorbent is evident from similar PSD for used sorbent, fines collection rate and no sorbent make-up
- Sorbent maintains excellent hydrodynamic / fluidization properties
- Good approach-to-equilibrium achieved in all reactor stages
- Quality data collected allowing for revision of economic analysis assumptions

Sorbent Working Capacity



Updated Economic Analysis

Breakdown of Main Contributors to Cost of CO_2 Captured



Preliminary Analysis

Summary

- *Basis*: DOE/NETL's Cost and Performance Baseline for Fossil Energy Plants – **updated with lab and bench-scale test data**
- Total cost of CO_2 captured ~ **45.0 \$/T-CO_2**
- 43.3 \$/T-CO_2 achievable through use of unproven spent sorbent scrubbing strategy
- Still represents **> 25% reduction** in cost of CO_2 capture, significant energy and capital savings compared to SOTA aqueous amine solvents

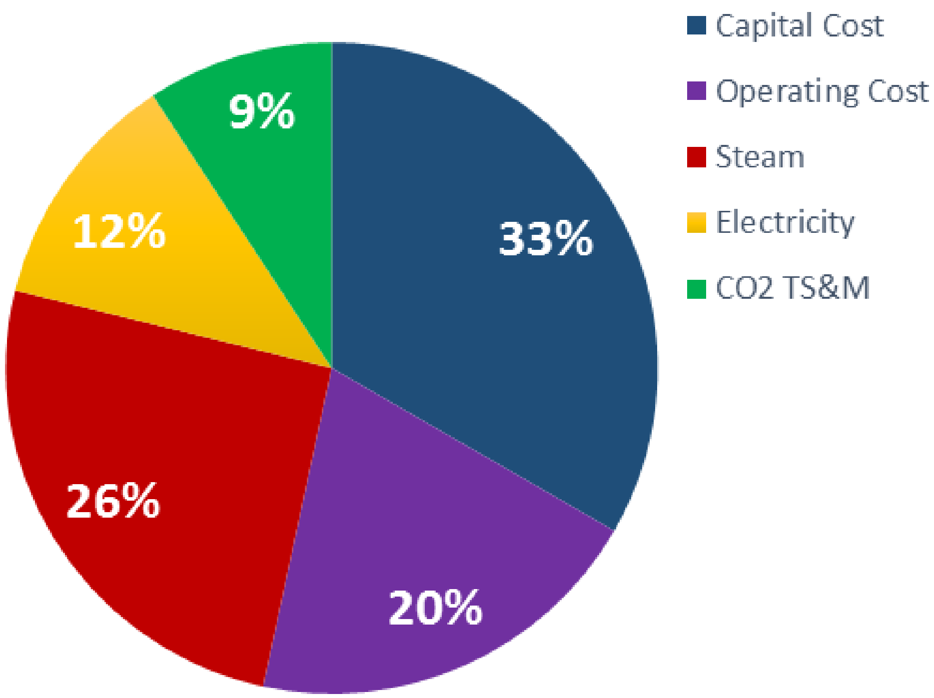
Main Factors impacting TEA

- Sorbent Cost
- CO_2 content in Regenerator
- Sorbent working capacity
- Regeneration temperature

Pathway to Cost Reductions

- Adsorber/Regenerator Design
- Heat recovery and integration
- Sorbent stability and cost

Updated Economic Analysis



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Technology Roadmap

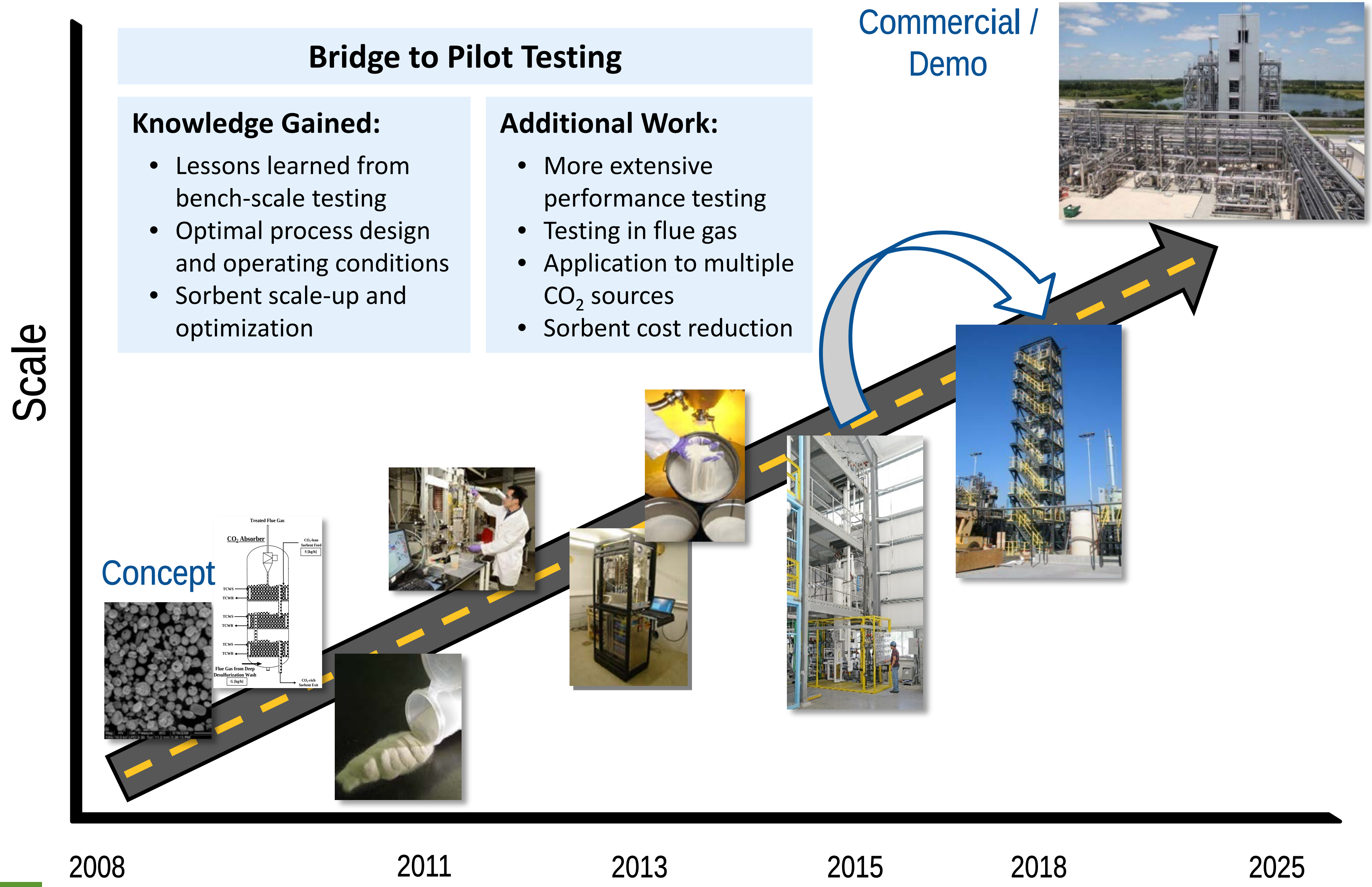
Bridge to Pilot Testing

Knowledge Gained:

- Lessons learned from bench-scale testing
- Optimal process design and operating conditions
- Sorbent scale-up and optimization

Additional Work:

- More extensive performance testing
- Testing in flue gas
- Application to multiple CO_2 sources
- Sorbent cost reduction



RTI-Norcem – Cement Plant Application

Objective

Demonstrate the technical and economic feasibility of RTI's advanced, solid sorbent CO_2 capture process in an operating cement plant

Period of Performance:

- 5/1/2013 to 12/31/2016

GASSNOVA

NORCEM
HEIDELBERGCEMENT Group

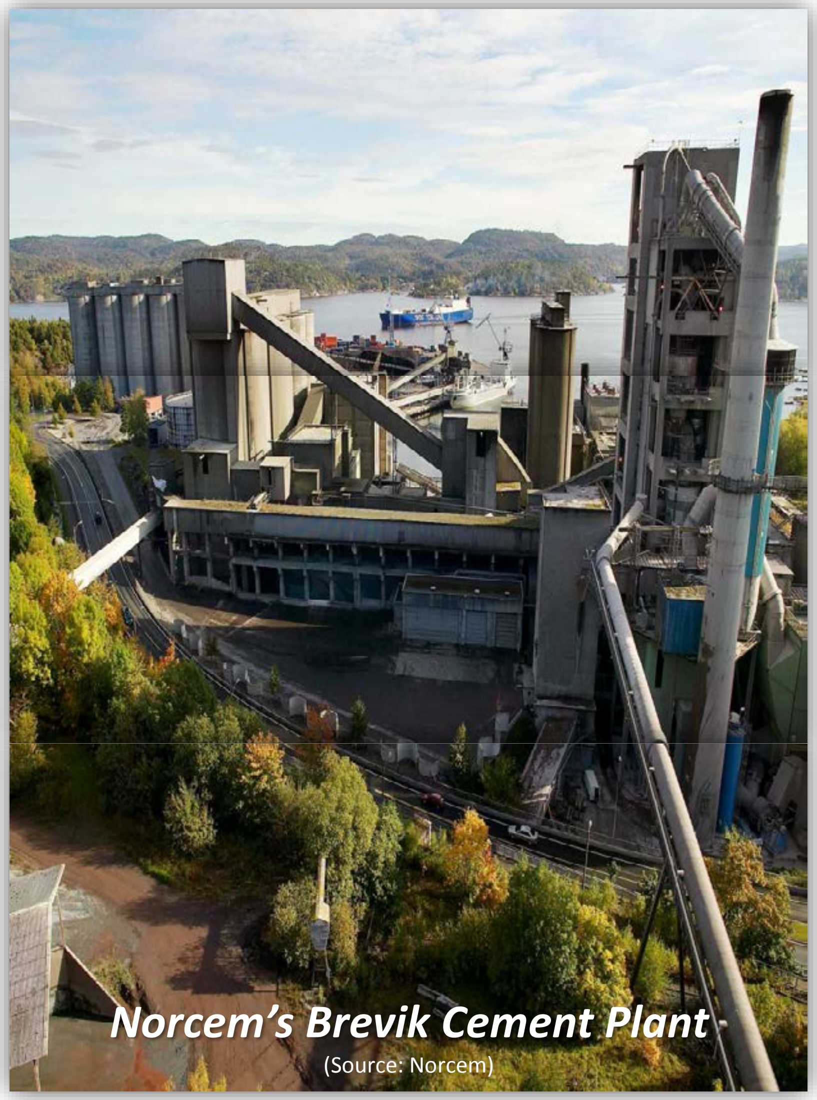
Two Phases

Phase I – Feasibility Review – *Complete*

- Sorbent exposure to actual cement plant flue gas
- Economic evaluation
- Commercial design for cement application

Phase II – Demonstration – *In Progress*

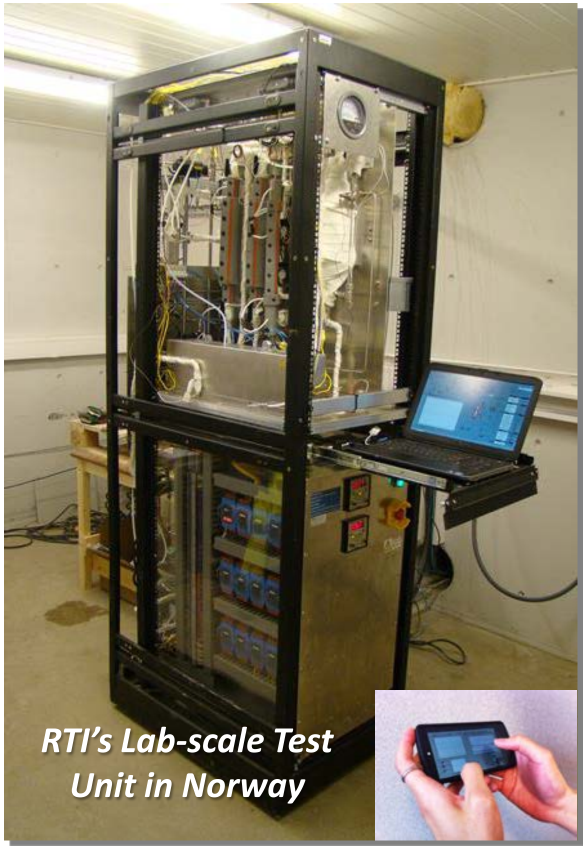
- Design, build, and test a prototype of RTI's solid sorbent CO_2 capture technology
- Evaluate CO_2 capture performance
- Update economics with pilot test data

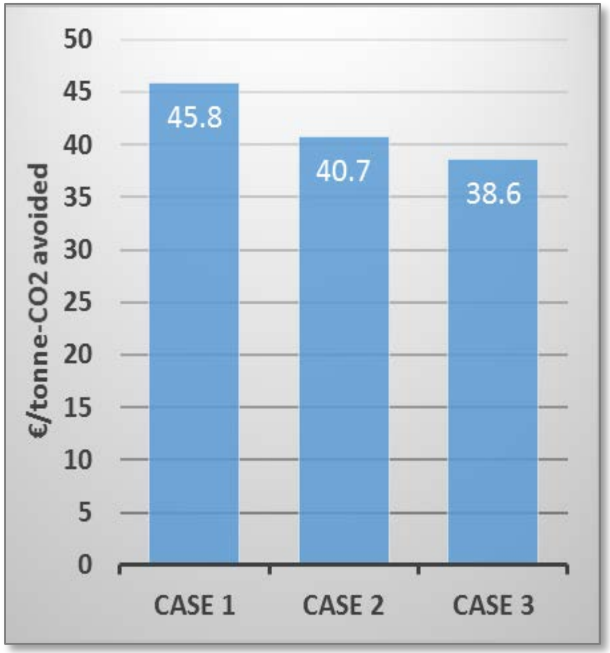


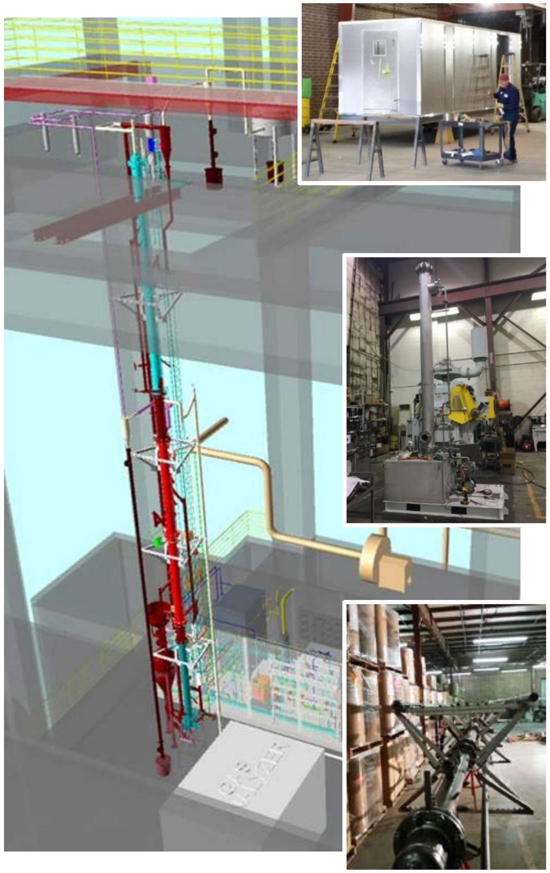
Norcem's Brevik Cement Plant

(Source: Norcem)

Progress and Lessons Learned


RTI's Lab-scale Test Unit in Norway





Testing

- Evaluated sorbent performance with actual cement flue gas
- No critical failure in performance over 300+ cycles. Achieved desired capacities

Economics

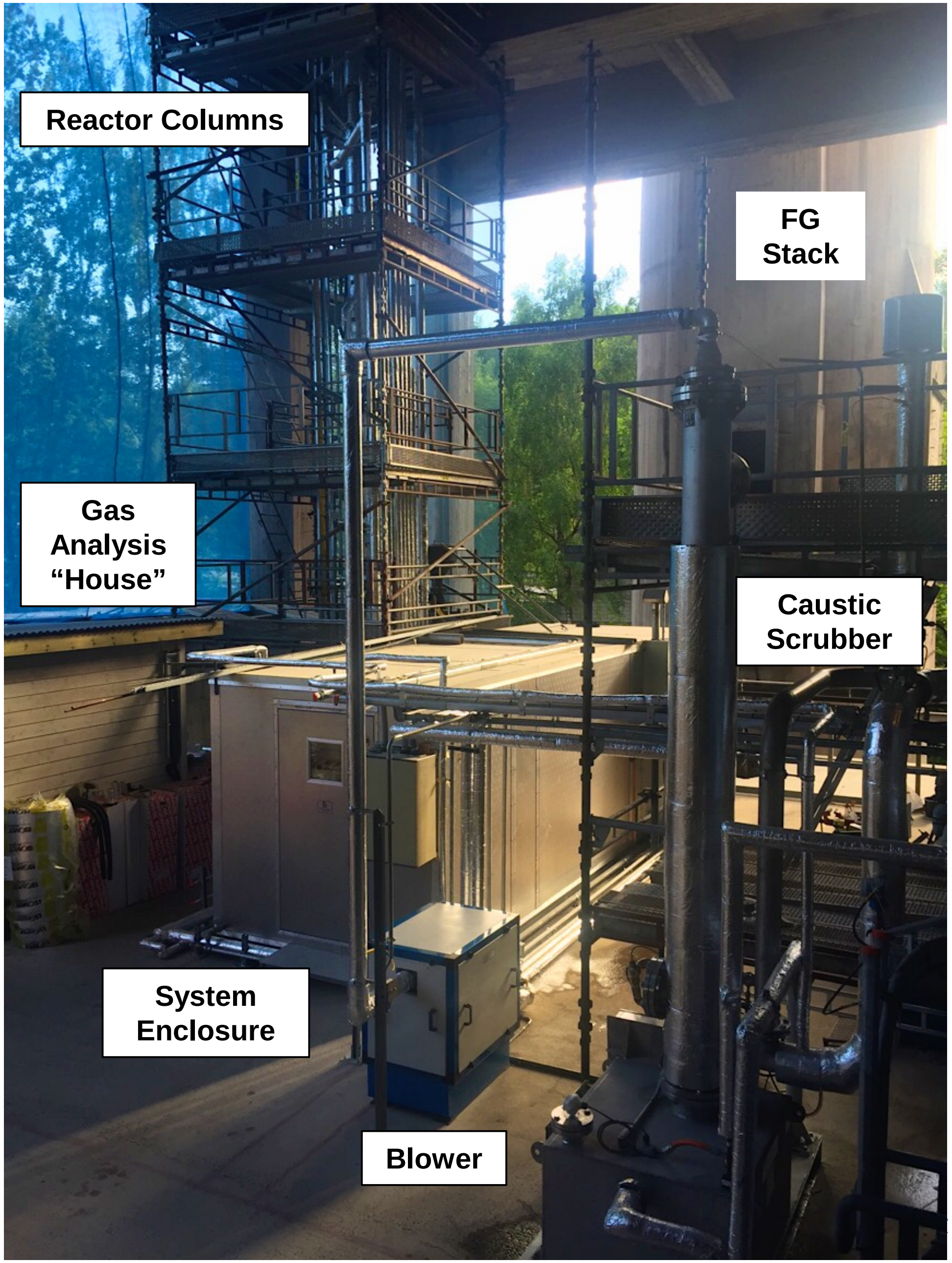
- Economic indicators of 38 – 46 €/t-CO_2 avoided show RTI's technology is economically competitive in CO_2 capture field
- RTI's technology is a good candidate for waste heat utilization

Pilot Design

- Design and engineering leveraged lessons learned on DOE-funded project
- Process Hazard Analysis
- Install complete

Phase II – Prototype Testing at Norcem


Test site in 2014



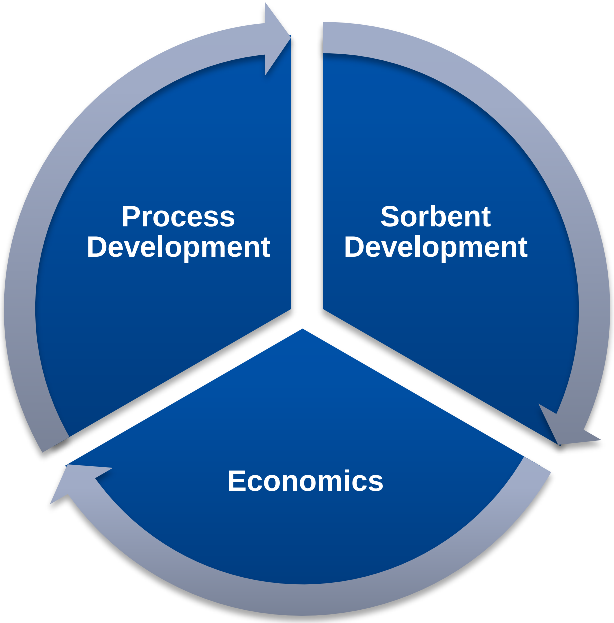
RTI Prototype

- **Completed:** Design, Engineering, Construction, Shipment, Installation, Commissioning, and Training
- Baseline and Parametric **testing currently underway** at Norcem’s cement plant
- Parametric and long-term performance testing planned **through Nov 2016**

Project Outcomes

Addressing Technology Challenges

- *Heat management*: Proved critical need for FMBR design through engineering analysis, lab-, and bench-scale testing
- Heat management technique in Bench system mimics commercial design
- *Solids handling*: improved sorbent working capacities, fluidizable material, and staged design reduce solids handling requirements
- Bench testing provided correlations to flow control, pressure balancing
- *Physical strength*: Bench testing proved excellent physical strength of fluidizable sorbent – very little attrition losses
- *Performance stability*: Excellent stability exhibited in bench testing
- Sorbent now has thermal-, chemical, and leaching-stability



Bridge to Pilot Testing

- Bench testing, lab screening, and modeling collected critical process design data for pilot design and detailed TEAs
- Economics are attractive with pathway to meet DOE goalls
- Sorbent manufacturing has been optimized – “Gen1” sorbent is viable path forward; Gen2 sorbents exhibit great potential
- Expanding potential market application through cement plant testing and NGCC evaluations
- Detailed economic assessments highlight areas for improvement:
  - Expanded data collection, novel heat integration, sorbent cost, sorbent working capacity, further staging studies

Technology Challenges

- Heat management / temperature control
- Solids handling / solids circulation control
- Physically strong / attrition-resistant
- Stability of sorbent performance

Acknowledgements

Funding provided by:

- The U.S. DOE/National Energy Technology Laboratory
  - Bruce Lani
  - Lynn Brickett
  - John Litinski
- Masdar (Abu Dhabi Future Energy Company)

RTI Team

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